THE STABILITY OF ENOLS

BY
NORMAN RABJOHN
B.S., University of Rochester, 1937
M.S., University of Illinois, 1939

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL
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THE STABILITY OF ENOLS

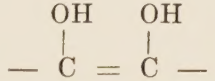
Introduction

The discovery that various *ortho* alkyl substituted diphenylacetylene glycols exhibit unusual stability has led to an extensive study of the relationship between structure and the tendency of a carbonyl compound to exist in the enolic state. The present investigation originated in an attempt to vary the nature of the *ortho* substituents in the diphenylacetylene glycols.

A natural extension of this study included the more interesting and little known derivatives of vinyl alcohol. In this connection two problems arose concerning the structures of two remarkably stable compounds. Because of the nature of the work, this discussion will be divided into three parts—the stable vinyl alcohol, 1,2-dimesityl-1-propene-1-ol (Part A); the stable enol, phenylmesitylvinyl alcohol (Part B); and an investigation of compounds related to 1,2-diphenylacetylene glycol (Part C).

Part A

In order to test whether the grouping



of substituted 1,2-diphenylacetylene glycols possesses a certain innate stability of its own, McKeever[1] carried out a synthesis which was designed to replace one of the enolic hydroxyl groups with an alkyl group. He treated desoxymesitoin with formaldehyde and obtained the desired ∝-mesitylvinyl mesityl ketone.

This unsaturated ketone readily absorbed hydrogen in the presence of platinum to yield a compound which was believed to be the stable vinyl alcohol 1,2-dimesityl-1-propene-1-ol. The structure of this substituted vinyl alcohol has been proven by a number of reactions, and several of its properties have been described. It has been ketonized to its isomeric form, ∝-mesitylpropiomesitylene, and several approaches to the preparation of this compound have been discussed.

Part B

The dehydration of glycols and more specifically of hydrobenzoins has been widely investigated by Tiffeneau[2] and a number of other workers. Several years ago Weinstock[3] treated 1,2-phenylmesitylethylene glycol with a dehydrating agent and obtained an unknown compound. Armstrong[4] isolated this same substance by the ozonization of 1,1-phenylmesitylethylene.

An extensive study of this most remarkable compound has been carried out in order to determine its structure. A number of reactions indicate that it is the stable enol, phenylmesitylvinyl alcohol. However, a certain amount of conflicting evidence points to a 1,2-diaryl substituted vinyl alcohol structure. It is believed that these results are due to molecular rearrangements. Many unusual transformations of this highly stable enol have been discussed.

Part C

Of all the enediols of the diarylacetylene glycol series so far reported, not one is known in which the ortho substituents are not alkyl groups. Likewise, no stable enediol has been prepared in which a heterocyclic or a hydroaromatic nucleus has replaced one or both of the aryl nuclei of a diarylacetylene glycol. Kohler, Jacobs, and Sonnichsen[5] have demonstrated that hexahydroacetomesitylene possesses properties similar to those of its aromatic homolog. It appears that there is little difference in the steric hindrance afforded by the mesityl and hexahydromesityl radicals in spite of the fact that the latter has lost its aromaticity.

This idea was applied to the enediols of the diphenylacetylene glycol type. 2,4,6-Triisopropylbenzoic acid was reduced catalytically to the hexahydro derivative. This was converted to the acid chloride and coupled by means of the binary mixture, $Mg + MgI_2$.[6] The resulting product was a mixture of isomeric diketones. Upon reduction, the mixture yielded a number of isomeric enediols which could not be separated.

The reduction of the dianil of mesitil has been shown to produce a substance which is believed to be an enediamine.

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VITA

The writer was born in Rochester, New York, on May 1, 1915. He attended the public schools of that city and was graduated from John Marshall High School in January, 1933. He enrolled in the University of Rochester in the fall of 1933 and in June, 1937 was awarded a Bachelor of Science degree. From June, 1937 to September, 1938 he was employed in the Research Laboratory of the Eastman Kodak Company. In the fall of this year he entered the University of Illinois and received a Master of Science degree in June, 1939. He held a teaching assistantship from 1939 to 1940 and a Röhm and Haas Research Assistantship from 1940 to 1942.

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